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1982/83 ST. CROIX RIVER WATER QUALITY REPORT

IWD-AR-WQB-83-49

INLAND WATERS DIRECTORATE
ATLANTIC REGION
WATER QUALITY BRANCH
MONCTON, NEW BRUNSWICK

1982/83 ST. CROIX RIVER

WATER QUALITY REPORT

IWD-AR-WQB-83-49

INLAND WATERS DIRECTORATE

ENVIRONMENT CANADA

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Atlantic Region

Moncton, New Brunswick

October 21, 1983

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LETTER OF TRANSMITTAL

Water Quality Branch
Inland Waters Directorate
Environment Canada
P. O. Box 861
Moncton, N. B.
October 21, 1983

Chairman, Canadian Section
IJC Pollution Advisory Board

Gentlemen:

Re: St. Croix River Water Quality Report 1982-83

This is the third annual report of the Water Quality of the St. Croix River, prepared by the Water Quality Branch, between Kellyland and Milltown.

The report concentrates on the Woodland - Milltown portion of the River and incorporates the data gathered from Monitoring of the River every 6 weeks by the Water Quality Branch as well as some data gathered by the United States Geological Service at their Automatic Water Quality Monitor at Milltown.

Observations and comments on this report would be welcome.

Yours sincerely,

D. H. Cullen, Chief
Water Quality Branch

ABSTRACT

This report presents the results of the 1982-1983 Saint Croix River water quality monitoring program. The effluent discharge from the Georgia-Pacific Paper Mill at Woodland is shown to have considerable effect on the water quality parameters of the lower reaches of the river. However, with the exception of total alkalinity, stations below Woodland generally complied with the Saint Croix water quality objectives and national water quality guidelines. Values of dissolved oxygen and pH on all occasions appeared to be such that passage of the Atlantic salmon into the lower reaches of the river was possible. Major ion concentrations were found to be well related to both river discharge and specific conductance. Specific conductance in the lower reaches was proposed as an indicator of river oxygen demand and was shown to be well related to percent saturation of dissolved oxygen.

RESUME

Ce rapport présente les résultats du programme d'investigations sur la qualité de l'eau de la rivière Saint-Croix pour 1982-1983. La canalisation de sortie de la Georgia-Pacific Paper Mill de Woodland se diversant dans la rivière démontre un effet considérable sur les paramètres de la qualité de l'eau de la section inférieure du cours d'eau. Tout de même, sauf pour l'alcalinité totale, les données des stations en aval de Woodland indiquent qu'elles sont généralement conformes aux objectifs visés pour la qualité de l'eau de la rivière Sainte-Croix et à celles du guide national de la qualité de l'eau. Les valeurs d'oxygène dissous et du pH, dans tous les cas apparaissent acceptables pour la montée du saumon de l'Atlantique dans la partie inférieure de la rivière. La concentration en ions majeurs s'avere être relativement relie au débit de la rivière et à la conductivité spécifique. La conductivité spécifique dans la section inférieure de la rivière est proposée comme un indicateur de la demande en oxygène pour la rivière et démontre être bien relie au pourcentage de saturation de l'oxygène dissous.

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INTRODUCTION

The International Joint Commission (I.J.C.) was established under the Boundary Waters Treaty of 1909 to mediate disputes and settle arguments concerning boundary waters and adjacent land dividing the U.S. and Canada. International issues are referred by either country to the I.J.C. which then establishes an international board to conduct any necessary technical studies. Upon completion, the findings of the studies are reported to the I.J.C. which then presents its recommendations on the issue to the appropriate country. The Advisory Board on Pollution Control in the Saint Croix River was established by the I.J.C. in 1966 to coordinate water quality planning and management efforts in the basin by both countries. With three members from Canada, three from the U.S. and one member at large, the Advisory Board on Pollution Control in the Saint Croix River has the responsibility of monitoring water quality in the river and of coordinating water quality planning activities. To assist the board in fulfilling its mandate, the Water Quality Branch conducts systematic water quality sampling in the International portion of the river to monitor the concentrations of toxic substances and other chemicals in the river water, as well as participating in the development of water quality objectives with particular reference to the passage of Atlantic salmon (salmo salar).

The study area is that part of the river which forms the international boundary between Canada and the United States. This

represents a reach of approximately 124 kilometers and drains much of York and Charlotte counties in New Brunswick and Washington county in Maine. In most of the watershed and for the upper 110 km of the Saint Croix River, the water quality is considered to be pristine. The region of water quality concern is a 14 km stretch between Woodland, Maine and Milltown, New Brunswick

The problem here is caused by a major industrial discharge at Woodland, Maine, and to a much lesser extent by municipal discharge and combined sewer overflows in Woodland and Baileyville, Maine. The Georgia-Pacific Corporation operates a Kraft Pulp Mill at Woodland, Maine, which produces fully bleached Kraft pulp, and discharges Kraft Mill effluent through a secondary waste treatment facility into the Saint Croix River. Although modifications to the plant and strict control on effluent and river discharge have served to greatly improve the water quality in the river since 1977, the 14 km stretch of river between Woodland and Milltown is still considered to be a water quality limited segment, although it is now of a quality such that it is capable of supporting an anadromous run of Atlantic salmon (salmo salar).

As part of the Water Quality Branch responsibility, an on-going project (ECS 1.1; WQB 11013) monitors the water quality of the Saint Croix River at a frequency of approximately six weeks, with the purpose of providing information on the long term impact of pulp mill waste on the water quality of the lower Saint Croix River. This report presents the findings of the Saint Croix River monitoring from April 1982 to

March 1983 and is similar in design to the 1979-1980 Water Quality Report (MS Report WQB-AR, January 1980) and the 1980 Water Quality Report (MS Report WQB-AR, April 1981).

METHODS

The Water Quality Branch of Environment Canada sampled the Saint Croix River on six occasions during the 1982-1983 study period. Samples were collected from eight stations located at Kellyland, Woodland, Baring and Milltown. At Baring and Milltown the river was sampled on the United States and Canadian shores as well as in mid-river in order to obtain information of the horizontal homogeneity of the water quality of the river.

In addition to the Water Quality Branch monitoring on the Saint Croix River, three other agencies (Water Resources Branch, Environment Canada; State of Maine, Department of Environmental Protection and USGS), sample the river.

In addition to conducting systematic grab sampling of river water for measurement of a wide range of water quality constituents at Milltown Heights, the U.S.G.S. also operates an Automatic Water Quality Monitor, which continuously measures four water quality parameters at this site.

Although these data will not be presented, some results from

sampling at Milltown by the WRB (Overview Network) and USGS (1982) will be incorporated into the figures in order to further elucidate water quality trends.

The Water Quality Branch sampling was conducted as outlined in the "Sampling for Water Quality" manual and the analytical methods are described in the January 1983 edition of the NAQUADAT dictionary. A list of the selected water quality parameters, their NAQUADAT codes and detection limits is presented in Table 1.

RESULTS AND DISCUSSION

The location of the selected sampling stations are indicated on Figure 1 while station NAQUADAT numbers and descriptions are presented in Table 2. The Kellyland station is located above the Woodland Mill outfall and thus is considered to indicate background or pristine conditions. The Woodland station gives an indication of the quality following initial dilution of the effluent after leaving the Georgia-Pacific Mill treatment plant. The six 1982-83 WQB sampling dates, along with river discharge and Woodland Mill BOD loadings are presented in Table 3.

The water temperatures, dissolved oxygen concentration and saturation, pH, specific conductance, water colour and total alkalinities for six dates at the Woodland, Kellyland, Baring and Milltown stations are presented in Tables 4 to 7 respectively. The major

ion concentrations of these stations are given in Tables 8 to 11, while the heavy metal concentrations are presented in Tables 12 to 15.

Since the effluent from the Woodland Mill enters the Saint Croix River on the United States side, major emphasis has in the past been placed on understanding the characteristics of the effluent plume and its subsequent incorporation into the river water mass. Previous results (MS Report WQB-AR, Jan., 1980; MS Report WQB-AR, April 1981) have indicated that the effluent plume travels down the United States side of the river remaining largely differentiated from the river water mass at the Baring sampling station. At the Milltown station, 4 km downstream, the effluent plume appears to be incorporated into the river water and there is little indication of any horizontal differentiation in water quality.

PHYSICAL PARAMETERS

This section will discuss the 1982-83 results for selected physical parameters (temperature, oxygen, specific conductance and water colour) at the eight Saint Croix River sample stations. A discussion of pH and alkalinity values will not be presented here, but will be considered briefly in the Water Quality Objectives and Guidelines section.

Water Temperature

Water temperatures at the Kellyland station ranged from 1.5°C

to 23.2°C during the study period and appear to follow ambient air temperatures. At Woodland, where effluent enters the system, water temperatures ranged from 10.2°C to 30°C and were from 2°C to 13°C greater than the background temperatures recorded at Kellyland. Baring water temperatures were similar to those at Kellyland and surprisingly there was no discontinuity across the river. It appears that there is sufficient travel time and turbulent motion between Woodland and Baring to allow the warmer plume water to equilibrate with ambient air temperatures as well as mix with cooler surface runoff entering the United States side of the river.

Dissolved Oxygen

The background station at Kellyland had oxygen concentrations ranging from 7.7 mg/L to 14.1 mg/L and on all occasions was close to saturation (92% to 104%). These saturation values fall well within the range of 86% to 120% saturation typical of oligotrophic Japanese waters (Yoshimura, 1938). At Woodland, oxygen concentrations had a range of 8.3 mg/L to 10.0 mg/L and percent saturations ranging from 92% to 103%. Below Woodland, due to the high oxygen demand caused by high organic load to the river, oxygen concentrations were considerably lower than background levels. At Baring, oxygen concentrations were often lower than at both Woodland and Kellyland having concentrations and saturations ranging from 6.0 mg/L to 13.8 mg/L and 72% to 102% respectively. At Milltown, oxygen concentrations were slightly lower ranging from 5.9 mg/L to 13.6 mg/L, and having a range of saturations

from 68% to 102%.

Specific Conductance

The Kellyland specific conductance values are characteristic of dilute, maritime region waters, ranging from 22 uS/cm to 32 uS/cm. At Woodland, the specific conductance values are both higher and more variable, with a range of 570 uS/cm to 2750 uS/cm. Downstream, at Baring, conductivities are indicative of the horizontal chemical discontinuity of the river previously described, with the highest values found on the U.S. shore. Baring specific conductances ranged from 39 uS/cm to 178 uS/cm at the U.S. station and 25 uS/cm to 92 uS/cm on the Canadian shore. At Milltown, the water mass was relatively mixed and the conductivity ranged from 30 uS/cm to 111 uS/cm.

Water Colour

In pristine condition, the Saint Croix River exhibits only slightly coloured waters, as indicated by the range of 10-40 Hazen units observed at the Kellyland station. The highly organic nature of the effluent at Woodland increases the water colour considerably with all values being much greater than 100 H.U. The downstream stations exhibited water colours intermediate to those found at Kellyland and Woodland with ranges of 30 to 100 H.U. and 35 to 100 H.U. at Baring and Milltown respectively.

MAJOR IONS

The results of the 1982-1983 sampling support previous observations on the mechanism of an effluent plume dispersion in the lower reaches of the Saint Croix River. At Baring, major ion concentrations (Table 10) are highest on the United States side and decreases across the river towards the Canadian shore. This trend is particularly noticeable for Na, Cl, SO_4, HCO_3 and specific conductance and to a somewhat lesser extent for Ca, K and organic carbon. The reach between Baring and Milltown allows for turbulent mixing of the water mass and the 1982-83 samples (Table 11) indicated that the Milltown water quality was horizontally homogeneous.

The major ion chemistry of the background site at Kellyland indicated that the Saint Croix River can, in a natural condition, be characterized as a calcium bi-carbonate system. On the six sampling occasions during the 1982-83 program the order of cation dominance (meq/L) was invariably Ca > Na > Mg > K while the anion order of dominance was HCO_3 > SO_4 > Cl. The sum of constituents ranged from 11.4 mg/L to 15.7 mg/L with a median value of 14.5 mg/L.

Below the Woodland Mill the major ion chemistry changes drastically, particularly on the U.S. side where the effluent enters the river. The dominant ions are Na and Cl originating from NaOH and NaOCl which are used extensively in the Kraft Mill and the CEHDE* bleaching process. The order of cation dominance was invariably Na > Ca > K > Mg

while the anion dominance was variable. Although Cl was always the dominant anion, SO_4 and HCO_3 interchanged as the second most abundant anion. The sum of constituents of the Woodland Mill water ranged from 293. mg/L to 1483. mg/L and had a median value of 1219. mg/L. The extreme increase in sum of constituents of this site relative to that observed at Kellyland shows the considerable effect that the Woodland Mill effluent has on water quality of the Saint Croix River. Also, the highly variable nature of specific conductance and sum of constituents at the Woodland site indicates that production at the mill and thus effluent discharge is highly irregular. A more detailed description of the processes used in the mill and the chemical procedures employed is given in Report IWD-AR-WQB-17 (April 1981).

At Baring, the effects of the effluent plume were still obvious. On the United States shore of the river at Baring, although much more dilute than observed at Woodland (sum of constituents; 19.5 mg/L to 87.2 mg/L), the dominant ions were Na and Cl. On the Canadian shore, Na was the dominant cation while the dominant anion was generally HCO_3. Further downstream at the Milltown station, water was more dilute (sum of constituents; 16.47 mg/L - 54.42 mg/L) with Na as the dominant cation and Cl and HCO_3 alternating as the dominant anion. Thus even at Milltown the Woodland effluent, although highly diluted, has shifted the Saint Croix River from a natural Ca, HCO_3 system to a Na; Cl; HCO_3 situation.

HEAVY METALS

With the exception of manganese and chromium, the trace metals in Tables 12 to 15 have water quality guidelines and thus concentrations of these parameters at particular locations will be discussed in more detail in the Water Quality Objectives and Guidelines section of this report.

At the Kellyland background station heavy metal concentrations were low, with levels of copper, lead, cadmium, mercury and chromium generally at the lower detection limit. Iron concentrations were less than 0.2 mg/L which is characteristic of only slightly coloured waters while concentrations of manganese were very stable and ranged from 0.01 mg/L to 0.03 mg/L.

As was seen for some of the physical parameters and the major ions, the Woodland Mill effluent also has elevated concentrations of selected heavy metals. This is particularly noticeable for aluminum, iron and manganese. Although these increased levels may be partially attributable to their direct usage in the pulp and paper process, there is also probably an association with the increased loading of organic matter into the Saint Croix River. Many metals such as aluminum, iron and manganese form complexes with organic ligands and thus elevated concentrations are often found in highly coloured organic waters. The other heavy metals are only slighly greater than those observed at the background station.

As was apparent for the major ion species, concentrations of aluminum, manganese and iron at the Baring stations were indicative of a non-mixed water mass. However, at Milltown, the concentrations of these parameters indicated that the river was in a well mixed condition. This adds further support to the contention that the Woodland effluent plume moves down the United States side of the river and is not completely mixed with the water mass until it reaches Milltown.

WATER QUALITY OBJECTIVES AND GUIDELINES

At present only three water quality objectives for the Saint Croix River exist. Two of these objectives are for dissolved oxygen (concentration and % saturation) and pH and were set to ensure passage of the Atlantic salmon. The third objective is for fecal coliforms and will not be considerable in this report. In addition, water quality guidelines for the protection of freshwater aquatic life have been set for several parameters by McNeely et al. (1979). A list of these guidelines as well as the two water quality objectives is given in Table 16. These objectives and guidelines will be discussed below. Numerous other parameters do not have either water quality objectives or guidelines.

Dissolved Oxygen

At no time during the 1982-1983 sampling period did grab samples

from any of the sites indicate dissolved oxygen concentrations or saturations below the Water Quality Objective for Fish Passage Designation. The lowest concentration (5.9 mg/L) was found on July 21, 1982 at Milltown on the United States side of the river. The U.S.G.S. AWQM at Milltown which recorded dissolved oxygen concentrations during the months of February, June, July, August and September, indicated that oxygen values ranged from 5.9 mg/L to 12.4 mg/L. As was the case for the grab samples these oxygen concentrations comply with the water quality objectives for the Saint Croix River.

pH

At no time during the 1982-1983 sampling program did the pH at any of the six stations on the Saint Croix River fall outside the limits of the water quality objectives for the river. The lowest value was a pH of 6.0 at Kellyland observed during high flow conditions in April of 1982. A pH range of 6.4 to 7.1 was recorded by the AWQM at Milltown during the October 1981 to September 1982 water year. This further supports the contention that the water quality objective for pH was not exceeded during the 1982-1983 study period.

Alkalinity

The suggested water quality guideline for total alkalinity is a concentration exceeding 20 mg $CaCO_3$/L. The samples from Woodland which have total alkalinities ranging from 67 mg $CaCO_3$/L to 301 mg

$CaCO_3$/L are the only ones which meet this guideline. Kellyland has total alkalinities ranging from 4.5 mg $CaCO_3$/L to 8.0 mg $CaCO_3$/L. Alkalinities at the mid-river stations of Baring and Milltown ranged from 5.0 mg $CaCO_3$/L to 14.0 mg $CaCO_3$/L and 5.0 mg $CaCO_3$/L to 15.5 mg $CaCO_3$/L respectively. This would suggest that the use of the 20 mg/L total alkalinity guideline for the Saint Croix River is presently unsuitable.

Aluminum

The guideline for aluminum concentration in natural waters is 0.100 mg Al/L, a value which has been adopted as the water quality objective for the International Saint John River Basin (ITAS; September 1980).

At Kellyland, all measured aluminum concentrations fall below the guideline value of 0.100 mg/L, and have a range of 0.02 mg/L to 0.088 mg/L with a median value of 0.057 mg/L. However, at the Woodland Mill, aluminum concentrations exceeded the guideline on all sampling occasions with a range of 0.6 mg/L to 5.9 mg/L and a median value of 3.0 mg/L. These high concentrations of aluminum are probably a consequence of the use of $(Al_2(SO_4)_3.18H_2O)$, alum, in the fresh process water treatment at the Georgia-Pacific Pulp Mill. At Baring the aluminum values were generally very near to the 0.100 mg Al/L guideline with the occasional high value, particularly on the U.S. side of the river. The range of Baring aluminum concentrations was 0.093 mg/L to 0.27 mg/L while the median value was 0.12 mg/L. The range of aluminum

concentrations at Milltown (.082 - 0.16 mg/L) was narrower than that observed at Baring, however the median value was identical (0.12 mg/L). Of the eighteen values presented for both Milltown and Baring (Tables 14 & 15) only 4 (22%) comply with the water quality guideline of 0.100 mg/L.

Cadmium

The recommended cadmium concentration guideline for the protection of aquatic life is 0.0002 mg/L. This value is five times lower than the detection limit of the technique presently employed to measure cadmium. At Kellyland, cadmium concentrations were below detection on all sampling dates. However, the process at the Woodland Mill seemed to affect the cadmium concentrations resulting in detectable values (.001 - .002; median = .0015 mg/L) on five of the six sampling dates. At both Baring and Milltown, cadmium concentrations were below detection on 13 occasions or for 72% of the samples. The range of values recorded was 0.001 to 0.002 mg/L for both stations.

As a large percentage of the measured values are at the detection limit and this limit is five times greater than the suggested guideline, there is an obvious need for the development of a more sensitive analytical technique. Until this is instituted, it will in most cases be impossible to compare the cadmium levels in the river to the suggested guideline.

Copper

The proposed guideline for copper in freshwaters is a concentration of 0.005 mg/L. This guideline is met on all but one occasion at the Kellyland station. This one date has the only copper concentration (.01 mg/L) which is above the detection limit of 0.002. As was the case for cadmium, the Woodland station is slightly enriched in copper relative to the background levels, having a range of concentrations of .002 to 0.005 mg/L with a median value of 0.0025 mg/L. However, these values do not exceed the guidelines on any occasion. Similar results were observed at the Baring stations which have detectable copper concentrations in six out of eighteen samples, all of which comply with the specified water quality guideline. At Milltown, all but three samples have copper concentrations which are below the analytical detection limit. These three detectable values were found in the U.S., mid-river and Canadian samples collected on March 31, 1983 and have concentrations of 0.006 mg/L, 0.009 mg/L and 0.007 mg/L respectively. These values all exceed the suggested guideline for copper, however, high copper concentrations in quality control blanks indicate that there was a sample contamination problem on this date.

Iron

Iron is a heavy metal which is commonly found in natural freshwaters, particularly those which are highly coloured. For this reason the suggested guideline is relatively high, allowing levels up to

0.300 mg Fe/L. The Kellyland iron concentrations ranged from 0.10 mg/L to 0.16 mg/L (median 0.12 mg/L) and thus were well below the suggested level. The range of iron concentrations at Woodland was 0.24 mg/L to 1.2 mg/L with a median of 0.69 mg/L and exceeded the guideline on all but one occasion.

The Baring Bridge iron concentrations complied with the guidelines on all but one occasion, having a range of 0.10 to 0.37 mg/L, and a median of 0.185 mg/L. Milltown exhibited a range (0.15 mg/L to 0.38 mg/L) and median (0.17 mg/L) similar to Baring, but exceeded the guideline on four occasions.

Lead

The water quality guideline for lead is set at a value of 0.03 mg/L which is considerably higher than any value measured at the Saint Croix River sampling stations. At Kellyland all lead concentrations were below the detection limit while at Milltown all values were either below or equal to the lower limit of detection concentration of 0.002. Lead concentrations at Woodland Mill ranged from 0.002 mg/L to 0.007 mg/L, being at worst 25% of the suggested guideline. Baring lead concentrations were below or at detection on 14 (88%) occasions and ranged from 0.002 to 0.004 mg/L.

Mercury

The suggested guideline for mercury is a concentration of 0.1 ug/L and all samples from the Saint Croix River complied with this value. In fact, mercury was not detected in any of the Saint Croix samples. The detection limit for mercury is 0.02 which is only 20% of the suggested guideline concentration.

WATER QUALITY - WATER QUANTITY RELATIONSHIPS AND TRENDS

The seasonal fluctuations in water quality of both rivers and lakes are often dependent on changes in hydraulic regime. Thus, there is generally a good relationship between discharge rate and chemical concentration, particularly those species which behave conservatively. Conversely, parameters which participate in chemical or biological reactions (i.e. alkalinity, nutrients) are likely to have little relationship to discharge.

As the modifying effect of discharge on a particular chemical constituent is often one of either dilution during high flow or concentration during low flow, the relationship is not always linear. For this reason, discharge concentration relationships presented in the literature often take a semi-logarithmic or logarithmic form (Lane, 1975).

Relationships between the logarithmic discharge rates and the logarithmic values of several selected chemical parameters for the Saint Croix stations have been considered. Although the small number of

observations make statistical analysis inappropriate, there are some obvious relationships. Figures 2, 3, and 4 indicate the relationships between Na, Cl and specific conductance with discharge rate respectively. The samples collected near the Woodland Mill outfall indicate that there is little relationhip between chemical constituent concentrations and the discharge rate of the Saint Croix River. This is to be expected as the concentrations of selected ions in the effluent depend on both the mill production rate and the type of processes in operation at the time of sampling. The background or Kellyland samples indicate that both Na and specific conductance values are very stable showing little variation with changes in flow. However, chloride concentrations at Kellyland are highly variable and are only poorly related to discharge rate. The use of Baring discharge data may not be suitable for the Kellyland data, as the Saint Croix is flow regulated at Woodland which is located in between Kellyland and Baring. However, use of Bailyville gauge data does not appear to improve the relationships.

At the stations downstream from the Woodland Mill (i.e. Baring and Milltown) there appears to be good relationships between discharge and Na concentrations (Figure 2) and discharge and specific conductance (Figure 4). However, the relationship between discharge and chloride concentration (Figure 3), at the Baring and Milltown stations was somewhat poorer than for the other two considered parameters. This can probably be explained by variations in output of chloride from the Woodland Mill. High amounts of chloride effluent are produced during the CEHDE* bleaching process but chloride compounds are not used in the

Kraft cooking liquor. Sodium is employed in both the Kraft Mill and the CEHDE* bleachery which may result in a more constant Na output and thus result in the better relationship observed for Na and discharge than was seen for chloride.

As a consequence of the small number of samples collected during the study period, the emphasis in the following discussion will be placed on the Milltown station which has additional data collected by technicians of WRB and the USGS. Figure 5 indicated that with the exception of one value (September 15, 1982), Milltown has a good relationship between discharge and specific conductance. The relationships between Na and discharge (Figure 6) and to a lesser extent chloride and discharge (Figure 7) were also good but once again the September 15, 1982 values were obvious outliers. Scrutiny of the ion chemistry for this September 15, 1982 sample indicated that there were no obvious contamination or analytical problem (Balance error = 6.3%) and thus the values obtained could not be ignored. In order to further understand the relationship between discharge and specific conductance at Milltown, data obtained from the AWQM (USGS, 1983) for the period of April 1982 to September 1982 inclusive, was analysed. This relationship is presented in Figure 8 and once again there appears to be a good discharge, specific conductance relationship. However, there is now a large number (30) of outliers (indicated by large dots) in the relationship, including the September 15, 1982 sample. All of these outlying values were measured during the month of September. Subsequent conversations with the Environmental Engineer of the Georgia-Pacific

Pulp Mill, confirmed that during 1982 the plant operation was stopped after Labour Day (September 6) for a period of approximately four weeks. Thus, these outlying values are indicative of the response of the Saint Croix River to a sudden cessation of effluent loading. Therefore, when considering the discharge-parameter concentration relationships for the Saint Croix presented here, it is essential to note that they are only valid during periods when the mill is in operation.

In addition to the relationships between discharge and chemical constituent concentrations, there are often relationships between the concentrations of selected parameters. As specific conductance gives an indication of total dissolved solids, there is often a good relationship between conductance and a specific major ion (i.e. Chloride, Sodium, Sulphate). Table 17 presents the linear regression analysis between sodium and specific conductance for the six sampling stations on the Saint Croix River. In all cases, except for the background station at Kellyland, there was a good relationship between specific conductance and sodium. Similar relationships were seen for conductance versus chloride concentration and conductance versus sulphate concentration. However, the regression co-efficients (r) were lower, particularily for sulphate, than those obtained for specific conductance and sodium concentrations. The relationships weakened considerably when less abundant (Ca, Mg, K, etc.) major ions were considered.

As specific conductance is related to both discharge and concentrations of major ions, it is possible that conductance may also

be a useful indicator of the non-conservative water quality parameters at the Saint Croix sampling stations. The parameter which is of the greatest concern for the quality of the Saint Croix River is the load of organic matter entering the river at Woodland and its subsequent effect on downstream dissolved oxygen concentration. If in fact specific conductance is a good indicator of the effluent organic load and therefore the oxygen demand of the system, a good relationship with dissolved oxygen would be expected. At Kellyland, the background station, as would be expected there, is only a poor relationship between specific conductance and oxygen saturation (Table 17). The same is true for the Woodland station where, although there is a high oxygen demand, there is not sufficient water residence time to have any effect on oxygen saturation. However, at the downstream stations, there is a good relationship between conductance and oxygen saturation. Although the number of observations included in the regression analysis is small, it does appear that specific conductance can be used as an indicator of dissolved oxygen saturation for the Milltown and Baring stations. Inclusion of Milltown data collected by WRB into the regression analysis does not significantly alter the regression co-efficient and even using AWQM data for the summer of 1982 (n=68) there is still a good relationship between specific conductance and oxygen saturation.

CONCLUSIONS

The background station at Kellyland indicates that the Saint Croix in pristine conditions is predominantly a Ca, HCO_3 river. However,

the effluent from the Georgia-Pacific Paper Mill at Woodland enriches the river in several major ions, particularly Na and Cl. This has shifted the natural ion dominance of the river, resulting in a Na, Cl and HCO_3 system. The results of the 1982-1983 Saint Croix River monitoring program, corroborate previous findings that the effluent plume moves down the United States shore of the river, is differentiated from the main river at Baring and is essentially mixed at Milltown.

With reference to water quality objectives, all of the grab samples and AWQM data for 1982, 1983 complied with the Saint Croix River objectives for dissolved oxygen and pH. With the exception of the Woodland station, none of the samples complied with the suggested total alkalinity guideline. A suggestion has been made to revise the alkalinity guidelines so that they will be more applicable to natural conditions in the river. The cadmium guideline was much lower than the detection limit of the technique presently in use and thus it was obvious that there is a need for the development of a more sensitive analytical technique. With the exception of the Woodland station, guidelines for several other parameters (Al, Cl, Fe, Pb, Hg) never or only occasionally were exceeded at the Saint Croix River stations.

Several water quality-water quantity relationships were investigated for the Saint Croix River stations. Major ion concentrations were, with the exception of Woodland and Kellyland, generally found to have a good logarithmic relationship with river discharge. However, these relationships assume that the Mill production

and effluent discharge are not interrupted. The effects of shutdown of the Mill are obvious from the specific conductance and discharge relationship at the Milltown station. Several relationships between selected water quality parameters were also investigated. Specific conductance was found to be a good indicator of conservative major ion concentrations for all stations except Kellyland. This was particularly true for the specific conductance relationships with the dominant ions in the effluent discharge (i.e. Na and Cl). The less dominant ions although still related to specific conductance, had significantly lower regression co-efficients. It was suggested that specific conductance may also be indirectly related to the concentration of organic discharge at Woodland and would therefore be indicative of the river oxygen demand. This was shown to be highly plausible as there was an excellent relationship between specific conductance and oxygen saturation at the Milltown and Baring stations.

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TABLE 1: A list of parameters, parameter codes and their detection limits

PARAMETERS	NAQUADAT PARAMETER CODE	DETECTION LIMITS
Temperature	02065S	-
Dissolved Oxygen (meter)	08102F	-
Dissolved Oxygen (Winkler)	08101F	10 ug/L
Specific Conductance	02042F	2 uS/cm
pH	10301F	-
Specific Conductance	02041L	0.2 uS/cm
pH	10301L	-
Colour	02011L	-
Turbidity	02073L	0.0
Total Phosphorus	15413P	5.0 ug/L
Nitrate & Nitrite	07110P	2.0 ug/L
Total Nitrogen	07601P	23. ug/L
Dissolved Organic Carbon	06107L	0.4 mg/L
Dissolved Inorganic Carbon	06051P	0.5 mg/L
Extractable Iron	26304P	50. ug/L
Extractable Manganese	25304P	10. ug/L
Extractable Copper	29305P	0.1 ug/L
Extractable Lead	82303P	1. ug/L
Extractable Aluminum	13305P	2. ug/L
Extractable Mercury	80315P	.02 ug/L
Extractable Cadmium	48302P	1. ug/L
Extractable Chromium	25303P	2. ug/L
Sodium	11103L	0.1 mg/L
Calcium	11103L	.04 mg/L
Potassium	19103L	0.1 mg/L
Magnesium	12107L	.005 mg/L
Chloride	17201L	0.1 mg/L
Sulfate	16304L	1.0 mg/L
Total Alkalinity	10101L	0.5 mg/L

TABLE 2: NAQUADAT Numbers and Site Descriptions of the Selected Sampling Stations on the Saint Croix River

NAQUADAT NUMBER	SITE DESCRIPTION
00NB01AR0013	Saint Croix River at Kellyland
00NB01AR0014	Saint Croix River, 200 m below Woodland Mill on the U.S. side of the river
00NB01AR0017	Saint Croix River at Baring RR Bridge - U.S. side
00NB01AR0018	Saint Croix River at Baring RR Bridge - Mid-river
00NB01AR0019	Saint Croix River at Baring RR Bridge - Canadian side
00NB01AR0020	Saint Croix River at Milltown Hwy Bridge - U.S. side
00NB01AR0001	Saint Croix River at Milltown Hwy Bridge - Mid-river
00NB01AR0021	Saint Croix River at Milltown Hwy Bridge - Canadian side

TABLE 3: Dates on which the Saint Croix River stations were sampled and the corresponding river discharge and Woodland Mill BOD loadings

SAMPLING DATES	RIVER DISCHARGE* CMS	WOODLAND BOD LOADING kg/dy
28-04-82	7770	6,175
02-06-82	1445	16,944
21-07-82	1094	5,835
13-10-82	1969	2,448
17-01-83	1550	9,447
30-03-83	3420	5,718

* Discharge at Baring USGS gauge

TABLE 4: Measurements of Temperature, Dissolved Oxygen, Specific Conductance, pH, Water Colour and Total Alkalinity on six dates for the Saint Croix River, 200 m below Woodland Mill on the United States side of the river (Station No. 00NB01AR0014)

DATE	TEMP. oC	OXYGEN mg/L	% Satn.	SP. COND. uS/cm	pH	COLOUR (H.U.)	ALKALINITY mg CaCO3/L
28-04-82	10.2	10.0	92	570	7.4	>100	67.
02-06-82	28.0	-	-	2750	7.7	>100	-
21-07-82	30.0	-	-	2200	7.2	>100	264.
12-10-82	18.5	9.4	86	1550	7.7	-	146.
19-01-83	15.3	8.3	103	2150	7.0	>100	257.
31-03-83	15.3	8.8	91	2400	7.5	-	301.

TABLE 5: Measurement of Temperature, Dissolved Oxygen, Specific Conductance, pH, Water Colour and Total Alkalinity on six dates for the Saint Croix River at Kellyland (Station No. 00NB01AR0013)

DATE	TEMP. oC	OXYGEN mg/L	% Satn.	SP. COND. uS/cm	pH	COLOUR (H.U.)	ALKALINITY mg CaCO3/L
28-04-82	8.0	11.8	103	22	6.0	35	4.5
02-06-82	19.0	8.4	93	26	6.7	30	5.5
21-07-82	23.2	7.7	92	31	6.4	10	7.2
13-10-82	10.5	10.5	97	29	6.6	10	8.0
19-01-83	-	-	-	32	6.5	40	5.7
30-03-83	1.5	14.1	104	30	6.4	30	5.8

TABLE 6: Measurements of Temperature, Dissolved Oxygen, Specific Conductance, pH, Water Colour and Total Alkalinity on six dates at three stations at Baring

DATE	STATION	TEMP oC	OXYGEN mg/L	% Satn	SP.COND. uS/cm	LAB pH	COLOUR (H.U.)	ALKALINITY mg CaCO3/L
29-04-82	US	7.5	11.8	102	39	6.3	35	6.0
	Mid-River	7.5	11.9	102	30	6.3	30	5.0
	Canada	7.5	12.0	103	25	6.3	30	5.0
03-06-82	US	17.5	6.7	72	156	7.0	100	24.5
	Mid-River	17.5	7.8	84	91	6.9	80	14.0
	Canada	17.4	7.9	85	76	6.9	70	12.5
21-07-82	US	23.3	6.0	72	178	6.8	100	17.7
	Mid-River	23.6	6.2	75	104	6.8	50	12.6
	Canada	23.6	6.1	73	92	6.7	50	11.2
14-10-82	US	11.5	9.8	93	80	6.2	50	5.5
	Mid-River	11.5	9.7	92	66	6.6	40	10.0
	Canada	11.5	9.8	93	50	7.1	40	9.5
19-01-83	US	-	-	-	128	6.6	100	14.6
	Mid-River	-	-	-	62	6.6	80	8.8
	Canada	-	-	-	58	6.6	70	8.2
31-03-83	US	2.0	12.6	94	90	6.8	88	11.1
	Mid-River	1.8	13.8	102	44	6.6	40	6.4
	Canada	1.7	13.8	102	40	6.5	35	6.4

TABLE 7: Measurements of Temperature, Dissolved Oxygen, Specific Conductance, pH, Water Colour and Total Alkalinity on six dates at three stations located at Milltown

DATE	STATION	TEMP oC	OXYGEN mg/L	OXYGEN % Satn	SP.COND. uS/cm	pH lab	COLOUR (H.U.)	ALKALINITY mg CaCO3/L
29-04-82	US	8.0	11.5	100	34	6.5	35	5.0
	Mid-River	8.0	11.7	102	32	6.2	40	5.0
	Canada	8.2	11.6	102	30	6.2	40	5.0
03-06-82	US	18.0	6.5	71	107	6.9	100	17.0
	Mid-River	17.5	6.9	74	105	6.9	80	15.5
	Canada	17.5	7.1	77	94	7.1	100	13.5
22-07-82	US	21.4	5.9	68	111	6.7	60	13.2
	Mid-River	21.4	6.0	70	110	6.6	100	12.9
	Canada	21.4	6.0	70	110	6.8	80	13.2
14-10-82	US	11.5	9.5	90	71	6.7	50	10.5
	Mid-River	11.5	9.7	92	69	6.5	40	10.5
	Canada	11.5	9.8	93	66	6.5	40	9.5
18-01-83	US	0.0	13.4	95	83	6.9	80	10.8
	Mid-River	0.0	13.6	96	74	6.5	80	9.9
	Canada	0.2	13.0	92	64	6.5	70	9.0
31-03-83	US	2.0	12.7	95	60	6.7	50	8.1
	Mid-River	2.0	12.8	96	57	6.7	50	7.7
	Canada	2.0	12.8	96	48	6.7	45	6.7

TABLE 8: Major Ion Concentrations (equivalents) for the Saint Croix River, 200 m below Woodland Mill on the U.S. side of the river. (Station No. 00NB01AR0014)

Date	Ca++	Mg++	K+ meq/L	Na+	Cl-	SO4=	HCO3-
28-04-82	.749	.115	.118	3.92	2.59	1.04	1.34
02-06-82	2.79	.370	.818	21.3	11.0	7.90	-
21-07-82	2.14	.380	.376	16.1	11.27	3.95	5.28
13-10-82	1.39	.288	.358	11.3	6.48	4.59	2.92
18-01-83	3.29	.395	.460	16.5	11.0	3.12	5.14
31-03-83	4.04	.420	.588	19.1	11.3	6.66	6.02

TABLE 9: Major Ion equivalent concentrations for the Saint Croix River at Kellyland (Station No. 00NB01AR0013)

Date	Ca++	Mg++	k+ meq/L	Na+	Cl-	SO4=	HCO3-
28-04-82	.120	.040	.008	.048	.028	.069	.090
02-06-82	.135	.038	.005	.052	.037	.058	.110
21-07-82	.170	.050	.003	.052	.037	.062	.144
13-10-82	.155	.057	.010	.052	.042	.064	.159
18-01-83	.172	.056	.008	.065	.056	.079	.114
31-03-83	.165	.059	.008	.057	.054	.102	.116

TABLE 10: Major Ion Equivalent Concentrations for the Saint Croix River at three stations located at Baring

Date	Station	Ca++	Mg++	K+	Na+	Cl-	SO4=	HCO3-
				meq/L				
29-04-82	US	.129	.040	.013	.178	.099	.100	.120
	Mid-River	.120	.039	.008	.104	.071	.079	.100
	Canada	-	.039	.005	.078	.056	.073	.100
03-06-82	US	.279	.060	.036	.957	.508	.385	.490
	Mid-River	.195	.049	.018	.435	.212	.210	.280
	Canada	.190	.047	.018	.391	.178	.183	.250
21-07-82	US	.349	.071	.031	1.044	.705	.302	.354
	Mid-River	.250	.058	.018	.565	.395	.183	.252
	Canada	.235	.058	.015	.478	.310	.166	.224
14-10-82	US	.130	.058	.031	.426	.206	.229	.110
	Mid-River	.200	.058	-	.309	.161	.177	.200
	Canada	.187	.057	.013	.270	.138	.156	.190
18-01-83	US	.334	.068	.026	.727	.508	.260	.292
	Mid-River	.212	.061	.013	.261	.172	.131	.176
	Canada	.207	.061	.013	.235	.158	.125	.164
31-03-83	US	.205	.062	.020	.492	.274	.212	.222
	Mid-River	.157	.058	.013	.178	.113	.115	.128
	Canada	.147	.052	.008	.144	.093	.119	.128

TABLE 11: Major Ion Equivalent Concentrations for the Saint Croix River at three stations located at Milltown

Date	Station	Ca++	Mg++	K+ meq/L	Na+	Cl-	SO4=	HCO3-
29-04-82	US	.120	.039	.013	.130	.085	.085	.100
	Mid-River	.120	.039	.010	.126	.082	.085	.100
	Canada	.120	.039	.010	.126	.082	.085	.100
02-06-82	US	.225	.054	.024	.565	.271	.252	.340
	Mid-River	.215	.053	.021	.522	.248	.235	.310
	Canada	.210	.054	.018	.435	.214	.208	.270
21-07-82	US	.254	.064	.018	.609	.395	.191	.264
	Mid-River	.250	.063	.018	.609	.423	.193	.258
	Canada	.260	.065	.018	.609	.423	.198	.264
14-10-82	US	.210	.060	.016	.347	.178	.198	.210
	Mid-River	.205	.062	.016	.344	.172	.187	.210
	Canada	.210	.062	.013	.269	.161	.177	.190
18-01-83	US	.237	.068	.015	.413	.257	.171	.216
	Mid-River	.232	.064	.015	.357	.243	.158	.198
	Canada	.212	.068	.013	.278	.189	.145	.179
31-03-83	US	.122	.058	.013	.292	.169	.158	.162
	Mid-River	.175	.062	.013	.265	.158	.156	.154
	Canada	.162	.057	.013	.196	.121	.125	.134

TABLE 12: Heavy Metal Concentrations for the Saint Croix River, 200 m below Woodland Mill on the U.S. side of the river (Station No. 00NB01AR0014)

Date	Fe	Mn	Cu mg/L	Pb	Cd	Al	Cr	Hg ug/L
28-04-82	.24	.45	<.002	.003	.001	0.6	<.0005	<.02
02-06-82	.85	1.9	.005	.007	<.001	3.6		<.02
21-07-82	.64	1.9	.003	.005	.002	2.7		<.02
13-10-82	1.2	1.4	.003	.002	.001	5.9		<.02
18-01-83	.74	2.0	<.002	.005	.002	3.4	.03	<.02
30-03-83	.61	1.8	.002		.002	2.6	.07	<.02

TABLE 13: Heavy Metal Concentrations for the Saint Croix river at Kellyland (Station No. 00NB01AR0013)

Date	Fe	Mn	Cu mg/L	Pb	Cd	Al	Cr	Hg ug/L
28-04-82	.10	.02	<.002	<.002	<.001	.088	<.0005	<.02
02-06-82	.10	.03	<.002	<.002	<.001	.050		<.02
21-07-82	.15	.03	<.002	<.002	<.001	.020		<.02
13-10-82	.16	.02	<.002	<.002	<.001	.03		<.02
18-01-83	.13	.02	<.002	<.002	<.001	.078	.0018	<.02
30-03-83	.11	.01	.010	<.002	<.001	.065	<.0005	<.02

TABLE 14: Heavy Metal Concentrations for the Saint Croix River at three stations on the Baring Bridge

Date	Station	Fe	Mn	Cu	Pb	Cd	Al	Cr	Hg
					mg/L				ug/L
28-04-82	US	<.10	.03	.003	.002	<.001	0.11	<.00005	<.02
	Mid-River	.13	.02	<.002	<.002	<.001	0.098	<.0005	<.02
	Canada	.12	.02	<.002	<.002	<.001	0.13	.0005	<.02
02-06-82	US	.37	.16	<.002	<.002	<.001	0.24		<.02
	Mid-River	.22	.09	<.002	<.002	<.001	0.13		<.02
	Canada	.20	.08	<.002	.002	<.001	0.12		<.02
21-07-82	US	.26	.18	<.002	.002	<.001	0.27		<.02
	Mid-River	.21	.11	<.002	.004	.001	0.12		<.02
	Canada	.23	.10	<.002	.003	<.001	.093		<.02
13-10-82	US	.21	.05	.002	<.002	.001	0.13		<.02
	Mid-River	.20	.04	<.002	<.002	.001	0.11		<.02
	Canada	.21	.04	.002	<.002	<.001	0.095		<.02
19-01-83	US	.18	.10	<.002	<.002	<.001	0.23	.0047	<.02
	Mid-River	.15	.04	<.002	<.002	<.001	0.13	.0018	<.02
	Canada	.15	.04	<.002	<.002	.002	0.13	.0017	<.02
30-03-83	US	.17	.05	.002	<.002	<.001	0.12	.0018	<.02
	Mid-River	.16	.03	.004	<.002	<.001	0.095	.0005	<.02
	Canada	.15	.03	.005	<.002	.001	0.11	<.0005	<.02

TABLE 15: Heavy Metal Concentrations for the Saint Croix River at three stations located at Milltown

Date	Station	Fe	Mn	Cu mg/L	Pb	Cd	Al	Cr	Hg ug/L
28-04-82	US	.14	.02	<.002	.002	<.001	0.11	<.0005	<.02
	Mid-River	.13	.48	<.002	.002	<.001	0.12	<.0005	<.02
	Canada	.12	.02	<.002	.002	<.001	0.11	<.0005	<.02
03-06-82	US	.35	.10	<.002	.002	<.001	0.16		<.02
	Mid-River	.25	.09	<.002	.002	<.001	0.15		<.02
	Canada	.25	.09	<.002	.002	<.001	0.15		<.02
21-07-82	US	.38	.11	<.002	<.002	<.001	0.14		<.02
	Mid-River	.36	.10	<.002	<.002	<.001	0.10		<.02
	Canada	.37	.10	<.002	<.002	<.001	0.13		<.02
31-10-82	US	.23	.04	<.002	<.002	<.001	0.12		<.02
	Mid-River	.23	.04	<.002	<.002	.001	0.10		<.02
	Canada	.25	.04	<.002	<.002	<.001	0.12		<.02
18-01-83	US	.17	.06	<.002	<.002	<.001	0.12	.0034	<.02
	Mid-River	.17	.05	<.002	<.002	.001	0.13	.0026	<.02
	Canada	.17	.04	<.002	<.002	<.001	0.13	.0025	<.02
30-03-83	US	.15	.04	.006	<.002	.002	0.095	.001	<.02
	Mid-River	.16	.03	.009	<.002	.001	0.11	.0009	<.02
	Canada	.16	.03	.007	<.002	.001	0.082	.0010	<.02

TABLE 16: Water Quality Guidelines and Objectives for Selected Water Quality Parameters

PARAMETER	OBJECTIVES	GUIDELINES*
Dissolved Oxygen	5 mg/L	
pH	6.0 - 8.5	
Alkalinity, as $CaCO_3$		>20 mg/L
Aluminum, as Al		<0.100 mg/L
Cadmium, as Cd		<0.2 ug/L
Copper, as Cu		<0.005 mg/L
Iron, as Fe		<0.300 mg/L
Lead, as Pb		<0.03 mg/L
Mercury, as Hg		<0.1 ug/L
pH		>6.5

* McNeely, R.N., V.P. Neimanis, L. Dwyer, 1979. Water Quality Sourcebook, Inland Waters Directorate, Ottawa, Canada.

TABLE 17: Linear Regression Analysis of Specific Conductance with several Water Quality Parameters for six stations on the Saint Croix River

Woodland	Cl = .00433 Sp. cond. +0.668	r = 0.96
Baring U.S.	Cl = .00430 Sp. cond. -.0975	r = 0.98
Baring Mid	Cl = .00372 Sp. cond. -.0591	r = 0.92
Baring Can	Cl = .00345 Sp. Cond. -.0412	r = 0.96
Milltown	Cl = .00349 Sp. cond. -.0455	r = 0.90
Kellyland	Cl = .00231 Sp. cond. -.0229	r = 0.79
Woodland	Na = .0081 Sp. cond. -0.891	r = 0.99
Baring U.S.	Na = .0064 Sp. cond. -0.079	r = 0.99
Baring Mid	Na = .0060 Sp. cond. -0.081	r = 0.99
Baring Can	Na = .0060 Sp. cond. -0.078	r = 0.98
Milltown	Na = .0059 Sp. cond. -0.079	r = 0.96
Kellyland	Na = .0012 Sp. cond. +.021	r = 0.73
Woodland	SO_4 = .0027 Sp. cond. -0.626	r = 0.84
Baring U.S.	SO_4 = .0016 Sp. cond. +0.64	r = 0.89
Baring Mid	SO_4 = .0016 Sp. cond. +.0438	r = 0.90
Baring Can	SO_4 = .0014 Sp. cond. +.0580	r = 0.85
Milltown	SO_4 = .0016 Sp. cond. +.0524	r = 0.89
Kellyland	SO_4 = .0014 Sp. cond. -.033	r = 0.32
Baring U.S.	O_2(%sat'n) = -0.237 Sp. cond. +112.3	r = -0.98
Baring Mid	O_2(%sat'n) = -0.369 Sp. cond. +115.8	r = -0.98
Baring Can	O_2(%sat'n) = -0.451 Sp. cond. +116.7	r = -0.98
Milltown	O_2(%sat'n) = -0.406 Sp. cond. +117.85	r= -0.95
Woodland	O_2(%sat'n) =0.0027 Sp. cond. + 88.57	r = 0.30
Kellyland	O_2(%sat'n) = -0.515 Sp. cond. +112.0	r = -0.34
Milltown (WQB & WRB)	O_2(%sat'n) = -0.373 Sp. cond. +115.5	r = -0.95
Milltown (AWQM)	O_2(%sat'n) = -0.335 Sp. cond. +108.3	r = -0.78

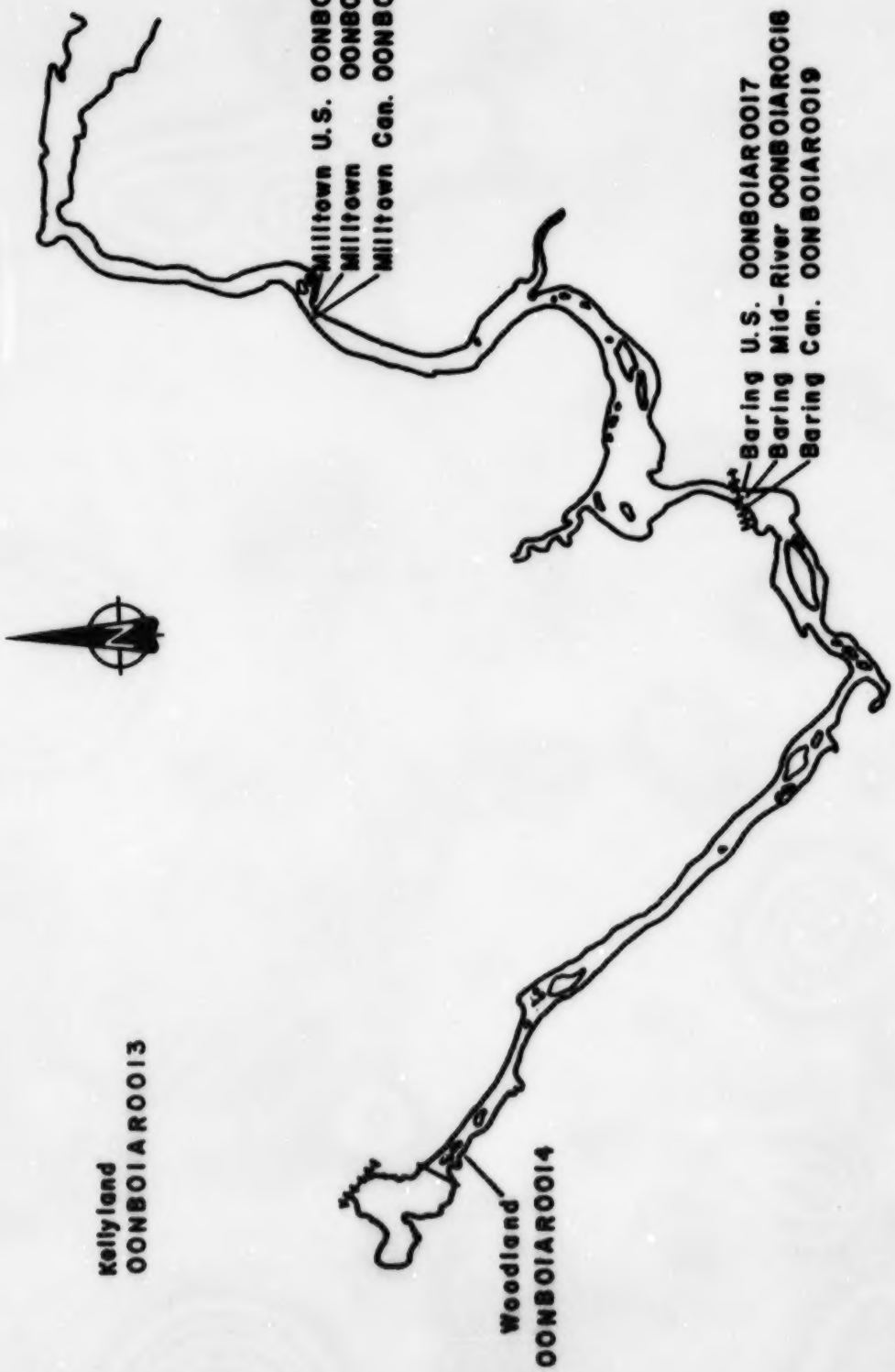

Fig. 1 Map of Study Area

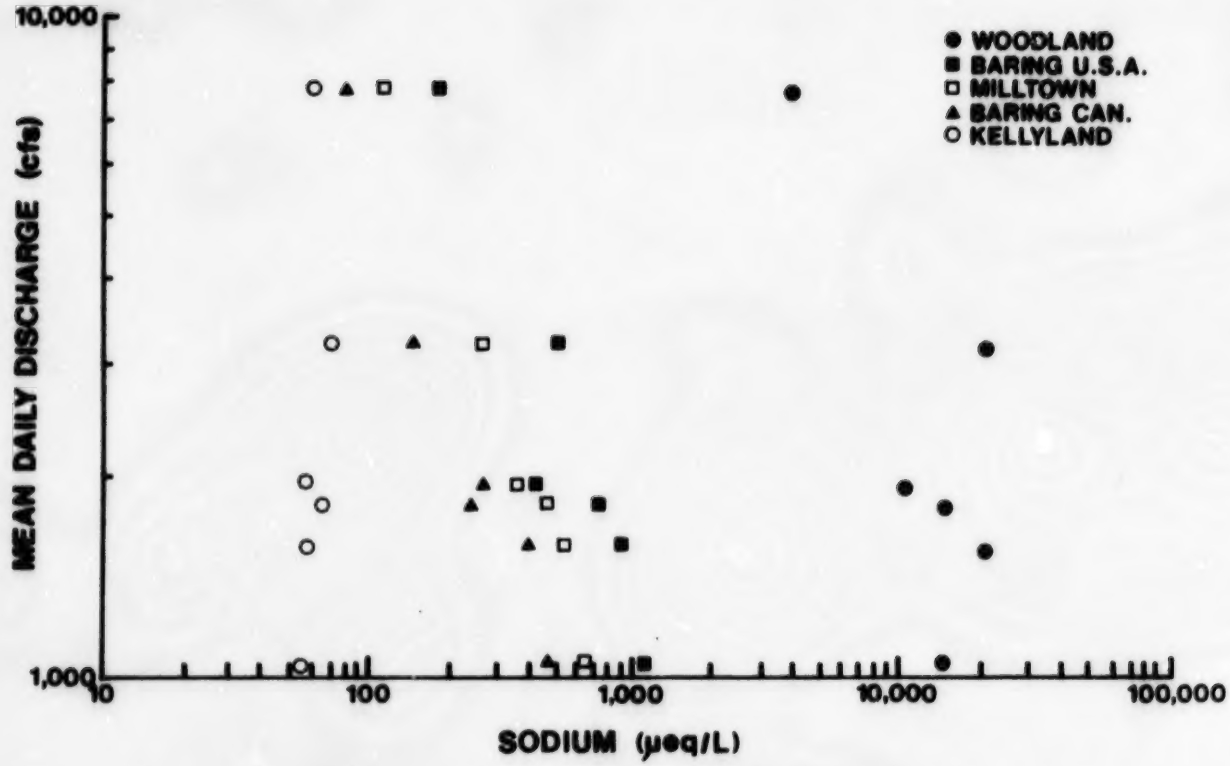

Fig. 2 Relationship between discharge and sodium concentration (µeq/L) for five St. Croix River sampling stations.

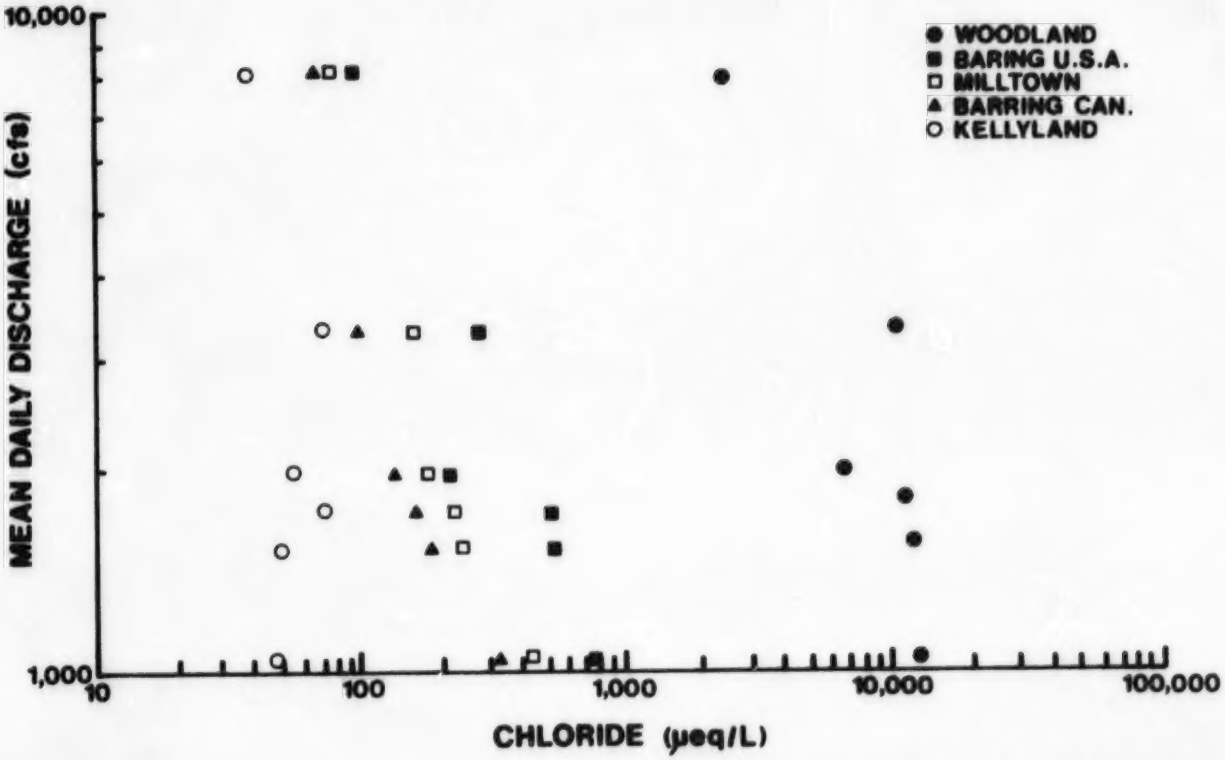

Fig. 3 Relationship between discharge and chloride concentration (µeq/L) for five St. Croix River sampling stations.

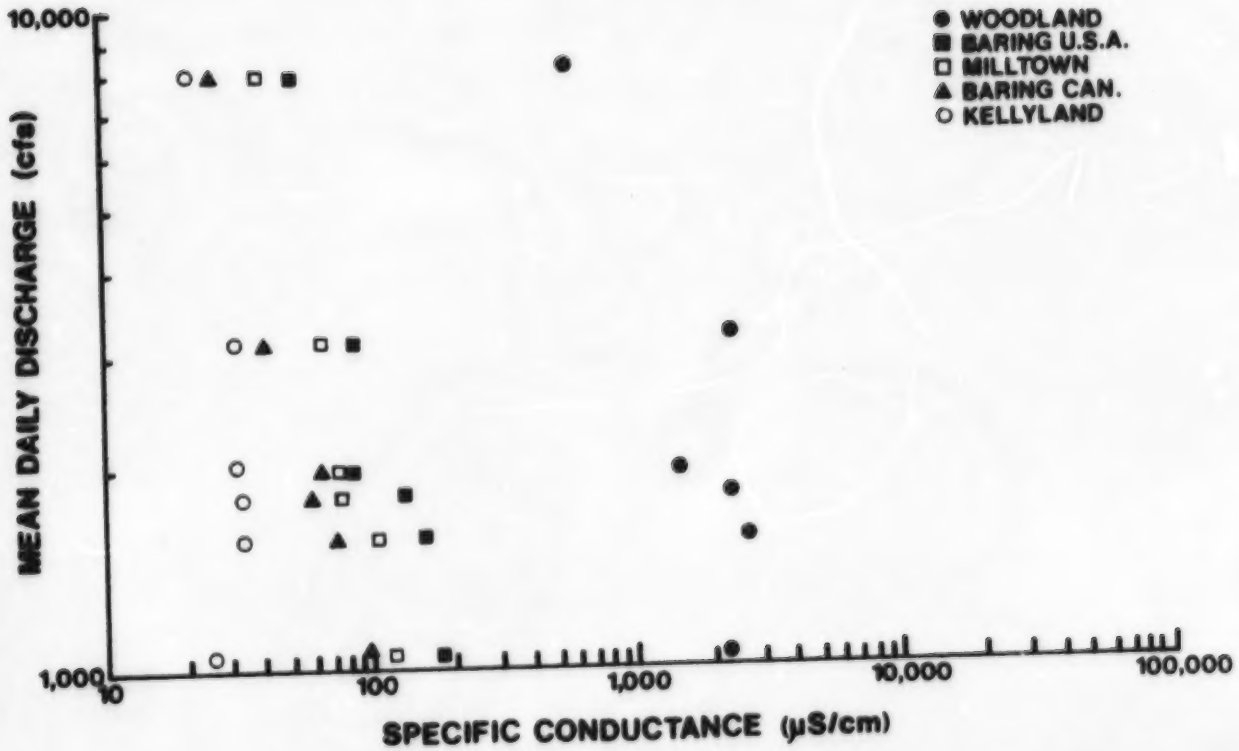

Fig. 4 Relationship between discharge and specific conductance for five St. Croix River sampling stations.

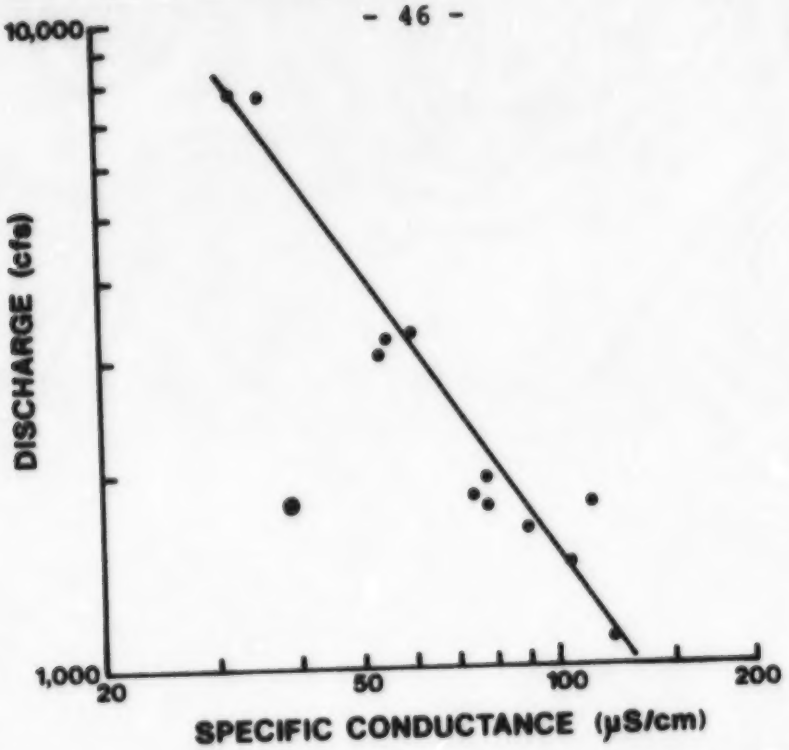

Fig. 5 Relationship between discharge and specific conductance for WQB, WRB, and USGS grab samples collected at Milltown.

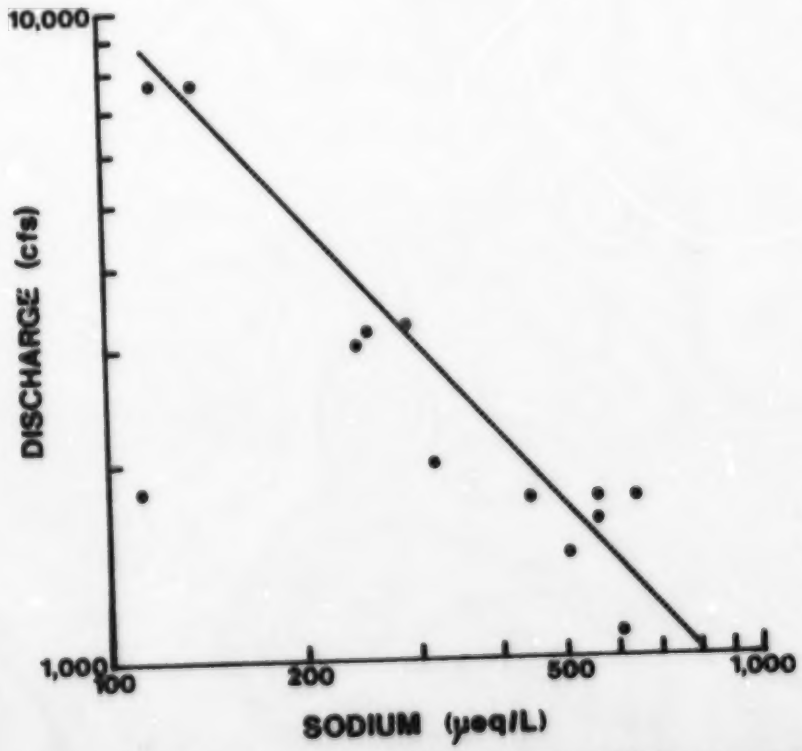

Fig. 6 Relationship between discharge and sodium concentration for WQB, WRB, and USGS grab samples collected at Milltown.

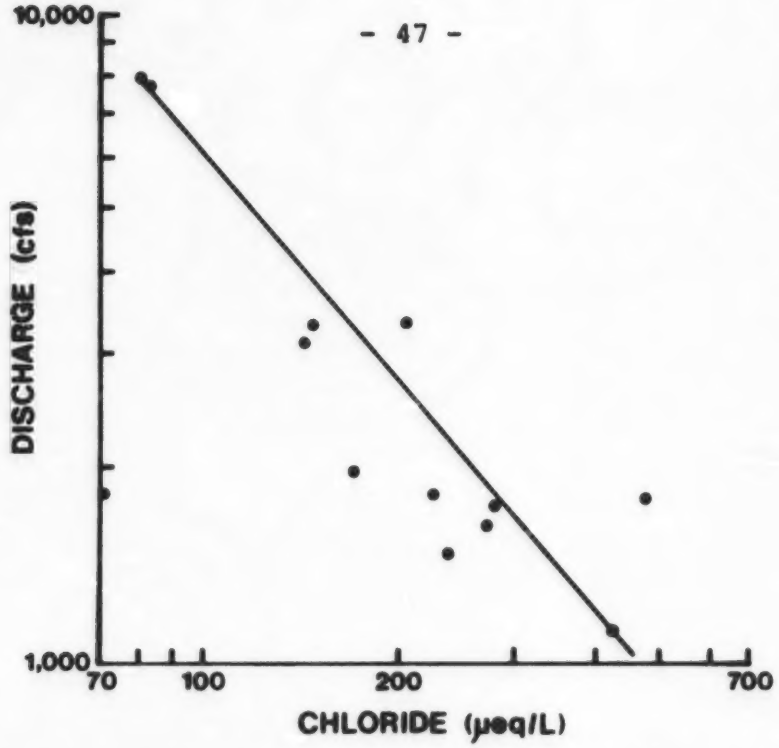

Fig. 7 Relationship between discharge and chloride concentration for WQB, WRB, USGS grab samples collected at Milltown.

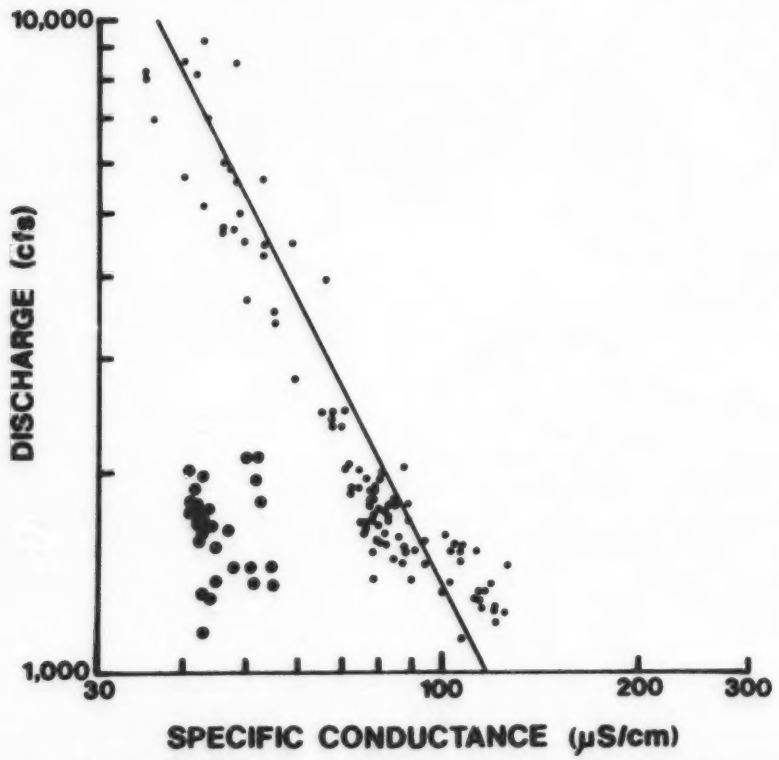

Fig. 8 Relationship between discharge and Milltown AWQM specific conductance measurements for the period April 1982 - Sept 1982.